

## Structural Characterization of Electrodeposited $\text{Bi}_2\text{Te}_3$ Thin film

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### ABSTRACT

The metallic layers of  $\text{Bi}_2\text{Te}_3$  Compounds and Their solid solution are the most common thermoelectric material system. One to good thermal properties around room temp. Bismuth telluride has been used for cooling devices and refrigerators. Thermoelectric cooling modules have been widely as integrated circuit packages. High power laser diodes and IR detectors be cope quick and precise control of temperature is possible with almost no noise during operation.

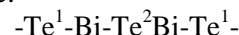
**Keywords:** Cyclic Voltammetry,  $\text{Bi}_2\text{Te}_3$ , Electrodeposition and XRD.

### INTRODUCTION

Bismuth telluride compounds and their solid solutions are the most common thermoelectric material system. Due to good thermal properties around room temperature, bismuth telluride has been used for cooling devices and refrigerators. Thermoelectric cooling modules have been widely utilized to cool electronic device such as integrated circuit packages, high power laser diodes, and IR detectors, because quick and precise control of temperature is possible with almost no noise during operation.

Bismuth telluride is a narrow gap semiconductor. It melts at  $580^\circ\text{C}$ . The  $\text{Bi}_2\text{Te}_3$  crystal possess a rhombohedral layered

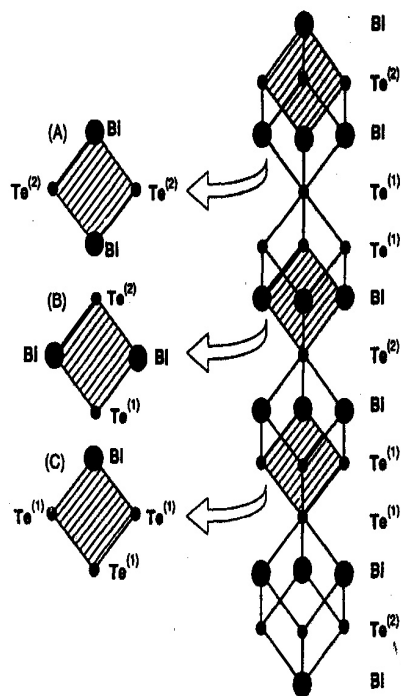
structure with space group  $R\bar{3}m$ . The crystal is composed of five atomic layers in the following sequence:



along c-axis. The superscripts refer to two types of bonding. The  $\text{Te}^1$  are bound by weaker Vander Waals force to the  $\text{Te}^1$  atoms of the adjacent tellurium layers and by mixed covalent-ionic bonds to the Bi atoms. Where as the  $\text{Bi}-\text{Te}^2$  bonds are covalent. It is easy to cleave the crystal along the c plane, as the mechanical strength is weak.

Taking into account the crystallographic structure of  $\text{Bi}_2\text{Te}_3$ , each atom has 3 neighbours in the upper plane and 3 neighbours in the lower one as the

hexagonal compact lattice in a direction perpendicular to the [111] direction. So we can represent the hexagonal cell by the stacking of cubes along their diagonal directions [111] as shown in fig.



**Fig -1 : Representation of the crystal structure of  $\text{Bi}_2\text{Te}_3$  by the stacking of cubes along their [111] directions.**

Since,  $\text{Bi}_2\text{Te}_3$  based single crystals are easily fractured through the cleavage plane during cutting process or during operation of the modules causing problems in the production yield and reliability of the modules. Thus investigations are focused on the processing technologies of the polycrystalline  $\text{Bi}_2\text{Te}_3$  based alloys. For improvement in mechanical strength, the sintered material has also been investigated.

The  $\text{Bi}_2\text{Te}_3$  crystals and compounds have anisotropic thermoelectric properties. The electric and thermal conductivity

verticals to direction of the c-axis are larger than the values along the parallel direction. The seeback coefficient shows only a slight difference in the anisotropy. The anisotropy ratio of electrical conductivity is about 4 for n-type and about 2 for p-type material. For the thermal conductivity the anisotropy is about 2 and 1.5 respectively.

Conventionally bismuth telluride alloyed with antimony telluride has been employed to form p-type thermoelectric material. The  $\text{Sb}_2\text{Te}_3$  compound possesses a similar rhombohedral structure as  $\text{Bi}_2\text{Te}_3$ . Usually some excess chalcogen such as Se, Te are also doped to control the carrier concentration in the material. The n-type doping of the bismuth telluride based alloys is generally accomplished by adding appropriate quantity of selenium.

Bismuth telluride crystals are commercially grown by Zochralski<sup>1-5</sup> or Bridgman<sup>6-12</sup> techniques. As already remarked, the van der Waal bonding of the successive Bi-Te planes in bismuth telluride imparts weak mechanical strength to the crystal, which can be easily cleaved along the c-planes. The poor mechanical strength has been one of the major drawbacks of bismuth telluride based TE coolers.

Recently preparation of thin film of  $\text{Bi}_2\text{Te}_3$  has also attracted considerable attention due to the need for miniaturization. Several approaches towards preparation of thin films of  $\text{Bi}_2\text{Te}_3$  have been attempted including physical evaporation<sup>13-16</sup>, flash evaporation<sup>17-19</sup>, cathodic pulverization<sup>20</sup>, solvothermal preparation<sup>21</sup>, electroless deposition<sup>22-23</sup>, and electrodeposition<sup>24-25</sup>. The electrodeposition technique using non-aqueous medium has been investigated by us and the results presented in this chapter.

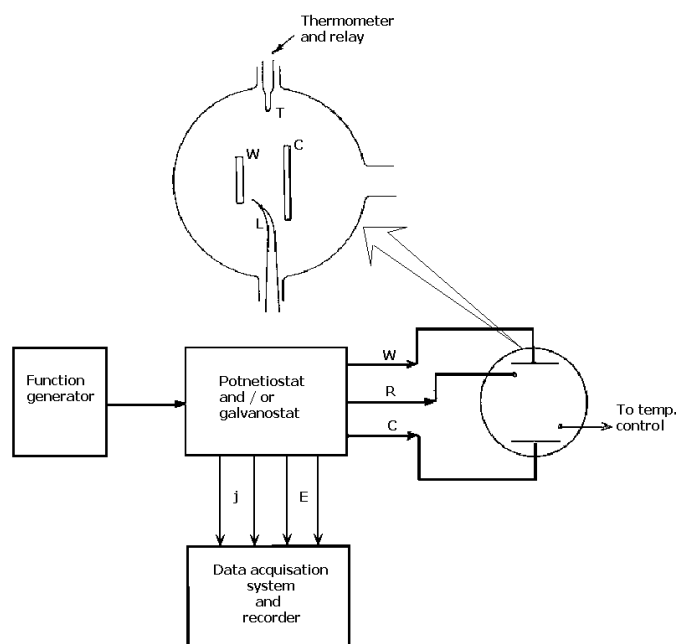
### EXPERIMENTAL DETAILS

The electrochemical investigation and electrodeposition of bismuth, tellurium as well as the compound semiconductor  $\text{Bi}_2\text{Te}_3$  was accomplished in a non-aqueous bath. The choice of the non-aqueous medium for electrodeposition was expected to offer following advantages:

- (a) Higher working temperature range up to  $190^\circ\text{C}$  as against below  $100^\circ\text{C}$  for aqueous medium.
- (b) Higher potential window. The aqueous medium offer limited range of working potential due to the hydrogen evolution reaction.
- (c) Higher solubility for selenium, telluride and antimony ion precursors. The aqueous

bath has limited solubility for tellurium and selenium salts. Moreover, antimony salts get hydrolyzed in aqueous medium. Thus growth of the ternary phase containing antimony, bismuth, tellurium alone with the dopants is not possible in aqueous medium. The non-aqueous bath chosen does not suffer from these disadvantages.

All electrochemical investigations were carried out in a glass cell using three-electrode geometry comprising of a working electrode of nickel, a platinum counter electrode and a saturated calomel electrode as the reference. All the electrodes were held in position using screw thread joints & Teflon seals. A typical electrodeposition arrangement has been shown in fig 2.



**Fig. 2 Schematic experimental arrangement for the study of the electrodeposition process (inset shows correct position of luggin tip).**

The backsides of the working and the counter electrodes were sealed by Teflon. The potential of the working electrode was maintained at a desired value using a programmable potentiostat model 362 (EG&G PAR USA). The electrolyte temperature was maintained constant within  $\pm 1^\circ$  using a temperature controller. Throughout the electrochemical investigations as well as electrodeposition, the electrolyte was moderately stirred with the help of a Teflon coated paddle and a magnetic stirrer. Ethylene glycol used as a solvent for electrodeposition, was first dried by passing through molecular sieves. The following electrolytic baths were investigated in the present studies.

#### **Electrodeposition of Bismuth Thin Film:**

2.42 gm  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 3 gm. Potassium Hydroxide (KOH) and 1gm tartaric acid dissolved in 50 ml of AR grade ethylene glycol.

Deposition of Bismuth on Nickel was accomplished at constant potential of  $-0.95$  Volts. The bath was continuously stirred throughout the deposition at a constant temperature of  $120 \pm 1^\circ\text{C}$ . The electrodeposition was allowed to continue for five minutes. The bismuth film was removed from the bath and then washed in water and dried. After drying, film was ready for Characterization.

#### **Electrodeposition of Telluride Thin Film:**

Tellurium film was deposited in a reaction matrix containing M/100 tellurium tetrachloride ( $\text{TeCl}_4$ ) solution in 50 cc volume of dry ethylene glycol.

Deposition of Tellurium on Nickel was accomplished at constant potential of  $-0.8$  Volt and  $120^\circ\text{C}$ . The bath was continuously stirred throughout the deposition. The electrodeposition was allowed to continue for five minutes. The tellurium (Te) film was removed from the bath and then washed in water.

Cyclic voltammetry was also performed in the above bath at  $120^\circ\text{C}$ . The voltammogrammes were recorded using a ramp rate of 5 mV/s and the cell current and the working electrode potential data was acquired using RS232 interface and computer.

#### **Electrodeposition of $\text{Bi}_2\text{Te}_3$ thin film:**

Bismuth Telluride films were deposited by preparing a reaction matrix containing 48ml M/10 bismuth nitrate solution and 2ml M/100 Tellurium chloride (IV) solution in ethylene glycol.

Deposition of Bismuth Telluride on Nickel (Ni) was accomplished under potentiostatic conditions at  $-0.9$  V and  $0.95$  V. The bath was continuously stirred throughout the deposition and the bath temperature was kept constant at  $(140 \pm 1)^\circ\text{C}$ . The electrodeposited films were washed with distilled water and dried.

The structure of the electrodeposited Bi and  $\text{Bi}_2\text{Te}_3$  films were investigated using X-ray diffraction. The details of the experimental arrangement employed have already been described in chapter 2.

### **RESULTS & DISCUSSION:**

#### **Cyclic Voltammetry of Bismuth**

A typical cyclic voltammogramme recorded in a bath containing M/10 bismuth solution has been shown in fig 3 The rest

potential of the Ni working electrode in the bath was  $-0.2\text{ V}$ . A sharp onset of cathodic current beyond  $-0.75\text{ V}$ , during the  $-ve$  sweep, as shown in the fig 3.3 indicated onset of reduction of  $\text{Bi}^{3+}$  ions. No other noticeable feature could be seen as the

cathodic scan was continued further beyond  $-0.75\text{ V}$ . The rapid increase in the cathodic current with increasing negative potential also suggested that the deposition of bismuth is mediated via a kinetically controlled charge transfer reaction.

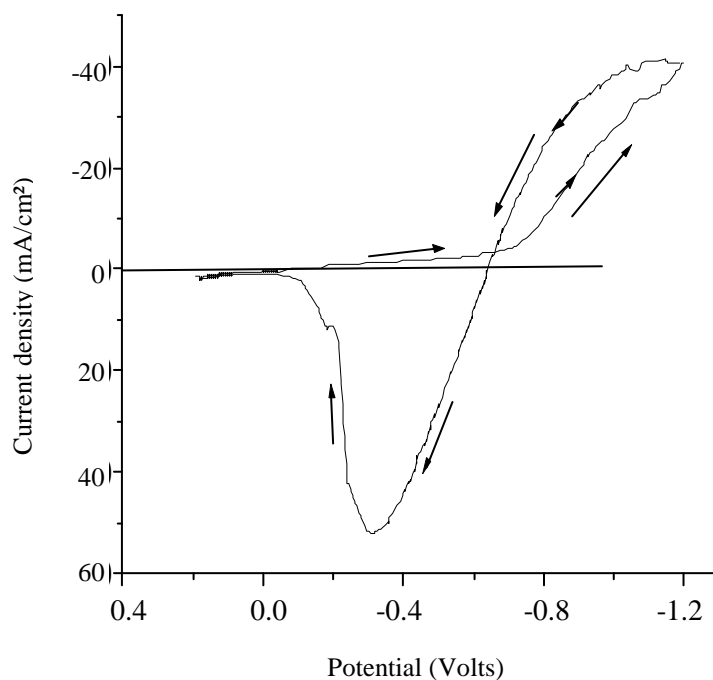


Fig-3 Cyclic voltammograms in a bath containing M/10 Bi in ethylene glycol at  $120^{\circ}\text{C}$  on nickel working electrode using ramp rate of  $5\text{ mV/s}$ .

Reversing the potential sweep in the positive (anodic) direction resulted in a cross over of the forward (cathodic) and reverse (anodic) sweeps at  $-0.63\text{ V}$ . Prior to the crossover in the more cathodic region of the reverse sweep, the current always remained higher compared to the corresponding value recorded during the forward sweep. Since the anodic sweep was recorded on the working electrode that was already coated with cathodically coated bismuth layer, the

observation of higher current during anodic sweep can be explained by assuming a lower deposition over potential for bismuth on nickel surface already coated with a bismuth film. The anodic sweep finally resulted into an anodic peak at  $-0.3\text{ V}$ , which can be correlated with the stripping of bismuth.

The slow scan cyclic voltammogram thus clearly indicate that bismuth can be electrodeposited in the bath at potential more negative to  $-0.75\text{ V}$ .

### Cyclic voltammetry of Tellurium ions:

Fig.4 shows slow scan (5 mV/s) cyclic voltammogram recorded in a bath containing M/100  $\text{TeCl}_4$  solution in ethylene glycol at  $120^\circ\text{C}$ . The working electrode was a nickel plate. Note that the cathodic current onset recorded at  $-0.5\text{ V}$  corresponded to the deposition of tellurium metal on nickel substrate. The cathodic current was seen to increase sluggishly beyond the onset potential indicating increased rate of reduction. The reverse sweep did not reveal any distinct peak except for a small wave at  $-0.69\text{ V}$ . Indicating that the deposition process for tellurium is irreversible.

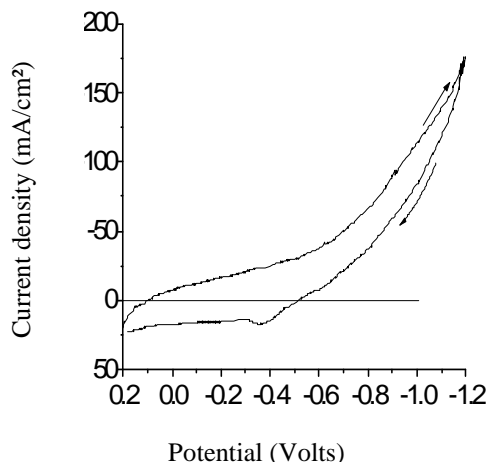


Fig- 4 Cyclic voltammograms in a bath containing M/100  $\text{TeCl}_4$  in ethylene glycol at  $120^\circ\text{C}$  on nickel working electrode using ramp rate of 5 mV/s.

### Cathodic polarization of Bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ):

The cyclic voltammogram recorded on nickel substrate in the bath containing M/10 bismuth nitrate and M/100

tellurium chloride (IV) in 50 ml of ethylene glycol has been shown in fig 3.6. The rest potential of the working electrode (Nickel) was  $-0.3\text{ V}$ . The cathodic sweep was continued from  $+0.25\text{ V}$  to  $-1.2\text{ V}$  using a ramp rate of 5 mV/s. The first cathodic onset recorded at  $-0.7\text{ V}$  corresponded to the reduction of tellurium ions at the working electrode.

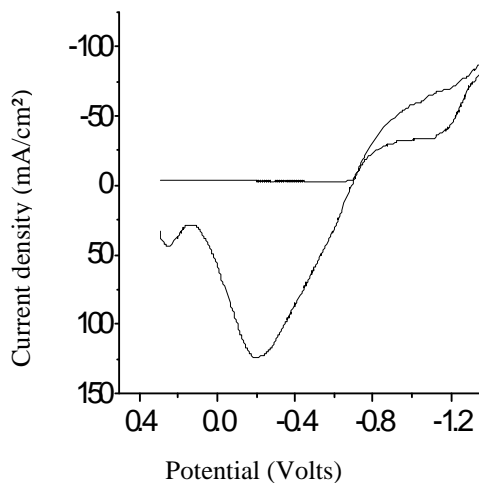


Fig-5 Cyclic voltammograms in a bath containing M/10 bismuth nitrate and M/100  $\text{TeCl}_4$  in ethylene glycol at  $140^\circ\text{C}$  on nickel working electrode using ramp rate of 5 mV/s.

The cathodic current was seen to rise rather sluggishly with increasing cathodic sweep before attaining a limiting value of approx ( $-32\text{ mA/cm}^2$ ). The observation of the cathodic current plateau between ( $-0.8\text{ V}$  to  $-1.1\text{ V}$ ) indicated that the reduction of tellurium occurs under the diffusion control.

The cathodic current was seen to increase again as the working electrode potential was swept to more negative value beyond  $-1.1\text{ V}$ . The rapid rise in the current

in this region indicated onset of kinetically controlled cathodic reduction of bismuth. The cyclic voltammogram recorded in the bath containing bismuth and tellurium ions thus indicate that tellurium is more noble as compared to bismuth i.e. the former deposition at more anodic potential. It will thus be possible to co deposit bismuth and tellurium from the single bath. Formation of the compound  $\text{Bi}_2\text{Te}_3$  is expected to occur at a potential that is more positive but close to  $-1.1$  V.

Potentiostatic deposition of the compound semiconductor film was therefore investigated for several potentials close to the bismuth deposition onset. The deposited layers were also investigated using XRD.

#### Structural Characterization of Electrodeposited Bi, Te & $\text{Bi}_2\text{Te}_3$ :

The observed X-ray diffraction pattern for a typical Bi film electrodeposited on Ni substrate at  $-0.95$  V, have been shown in fig 6. The observed peak position  $2\theta$ , intensities, FWHM and the calculated d-values have been summarized in the table 3.1 along with the standard values. The most prominent reflection was recorded at  $2\theta=27.158^\circ$  corresponding to the (012) planes of rhombohedral bismuth. Other reflections implying growth of rhombohedral phase of bismuth could also be seen at  $2\theta = 22.460^\circ, 37.974^\circ, 39.618^\circ, 44.553^\circ, 46.007^\circ, 48.684^\circ$ , corresponding to (003), (104), (110), (015), (113) and (202) reflections of bismuth respectively. The experimentally determined d values were found to be in close agreement with the standard JCPD values as shown in table (1)

Bismuth is known to possess a rhombohedral primitive cell with space group  $R \bar{3}m^{26}$  or a cubic structure with space group  $Im3m^{27}$ . The rhombohedral primitive cell can however be indexed as a non primitive hexagonal lattice with the miller indices (hkl) using the following relationship.

$$h = H - K \quad (3.1)$$

$$k = K - L \quad (3.2)$$

$$l = H + K + L \quad (3.3)$$

where (H,K,L) refers to rhombohedral axes. Thus the powder pattern of a rhombohedral substance is often indexed on a hexagonal Hull-Davey or Bunn chart. The true nature of the lattice can be recognized using equation 3.1 to 3.3, which when combined together yield

$$-h + k + l = 3n \quad (3.4)$$

So that for a really rhombohedral lattice n being an integer, the sum  $(-h + k + l)$  will always be an integral multiple of 3. From table 1 it is obvious that the sum  $(-h + k + l)$  always satisfies this relationship, thereby, implying that the electrodeposited material corresponds to a polycrystalline phase of rhombohedral bismuth.

The lattice parameters for the rhombohedral system  $a_R$  can be related to the corresponding parameter for the hexagonal lattice ( $a_H$ ) by the following relationship.

$$a_R = \frac{1}{3} \sqrt{3a_H^2 + c^2} \quad (3.5)$$

$$\sin \frac{\alpha}{2} = \frac{3}{2 \sqrt{3 + \left(\frac{c}{a_H}\right)^2}} \quad (3.6)$$

We calculated  $a_H$  and  $c$  from the observed XRD data using the following relationship.

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a_H^2} \right) + \frac{l^2}{c^2} \quad (3.7)$$

The average values of  $a_H$  and  $c$  were obtained as 4.546 Å and 11.864 Å respectively, for which  $a_R$ ,  $\alpha$  for the rhombohedral system was also calculated as 4.746 Å and 57.23 Å respectively.

The primitive cell in a Bismuth telluride crystal is rhombohedral. However, the structural assignment of the unit cells is often carried out by assuming a hexagonal non-primitive cell. Phase assignment of the electrodeposited Bi<sub>2</sub>Te<sub>3</sub> films in the present study, was, therefore, carried out using the standard JCPD data for hexagonal lattice.

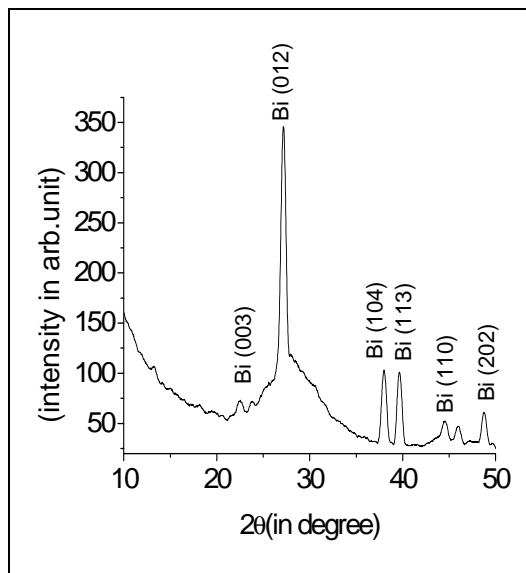


Fig- 6. Typical GAXRD data recorded for Bismuth film electrodeposited at -0.90 V on nickel.

Table 1

The observed values of  $2\theta$ ,  $d$ , FWHM and peak intensities along with the standard values for bismuth films.

| S. no | $2\theta$ | $d$ (Å)   |          | FWHM degree | Intensity |          | (Hkl) |
|-------|-----------|-----------|----------|-------------|-----------|----------|-------|
|       |           | Standard. | Observed |             | Standard. | Observed |       |
| 1.    | 27.158    | 3.280     | 3.289    | 0.522       | 100       | 100      | (012) |
| 2.    | 37.974    | 2.369     | 2.369    | 0.388       | 27        | 28       | (104) |
| 3.    | 39.618    | 2.273     | 2.273    | 0.400       | 29        | 28       | (110) |
| 4.    | 44.553    | 2.032     | 2.034    | 0.650       | 5         | 5        | (015) |
| 5.    | 46.007    | 1.971     | 1.969    | 0.2153      | 6         | 6        | (113) |
| 6.    | 48.684    | 1.868     | 1.869    | 0.353       | 13        | 13       | (202) |

A typical diffraction patterns for the bismuth telluride film electrodeposited at -0.95 V and -0.90 V have been shown in fig. 8 & 9 respectively. The peak assignments including  $2\theta$ ,  $d$ , FWHM and peak intensity as well as the Miller indices for the two film have been summarized in table 3 & 4 respectively along with the standard value for comparison. Note that the observed XRD

reflections are indicative of growth of a polycrystalline phase. . In case of Bi<sub>2</sub>Te<sub>3</sub> film grown at -0.95 V, sharp reflexes were recorded at  $2\theta = 27.126^\circ$ ,  $37.936^\circ$ ,  $39.605^\circ$ ,  $44.648^\circ$ ,  $48.700^\circ$  and  $56.00^\circ$ , corresponding to  $d$ -values of 3.28, 2.36, 2.27, 2.02, 1.86, and 1.64 Å respectively. All the  $d$  values matched closely with the corresponding standard values as shown in table 3. The



observed peaks in the XRD patterns of the bismuth telluride film electrodeposited at  $-0.90$  V were also Similar except that reflexes at  $2\theta=27.94^\circ$  was also seen in this sample.

A comparison of the relative peak intensity for the two samples of bismuth telluride indicated a difference in the texture of the two films. While both the films were found to grow with a strong (015) orientation the degree of orientation was much higher in case of the films grown at  $-0.90$  V.

The grain size in the bismuth telluride film was calculated by the line broadening of the characteristic reflexes of

the diffraction pattern and the Scherer's formula

$$t=0.9\lambda/B\cos\theta \quad (3.8)$$

The average grain size were found to  $212 \text{ \AA}$  and  $332 \text{ \AA}$  respectively for the film electrodeposited at  $-0.95$  &  $-0.90$  V. Obviously the lower electrodeposition potential yielded deposits with slightly large grain size and higher degree of orientation.

The lattice parameters for the rhombohedral lattice of bismuth telluride were also calculated by a procedure similar to the one adopted for bismuth.

**Table 2**  
The observed values of  $2\theta$ ,  $d$ , FWHM and peak intensities along with the standard values for  $\text{Bi}_2\text{Te}_3$  films electrodeposited at  $-0.90$  V.

| S. no. | $2\theta$ | $d \text{ (\AA)}$ |          | FWHM (degree) | Relative Intensity |          | (hkl)    |
|--------|-----------|-------------------|----------|---------------|--------------------|----------|----------|
|        |           | Standard.         | Observed |               | Standard           | Observed |          |
| 1      | 27.142    | 3.23              | 3.282    | 0.378         | 100                | 100      | (0 1 5)  |
| 2      | 37.97     | 2.360             | 2.367    | 0.441         | 70                 | 18       | (1 0 10) |
| 3      | 39.654    | 2.21              | 2.271    | 0.433         | 50                 | 18       | (1 1 0)  |
| 4      | 45.996    | 1.996             | 1.971    | 0.552         | 30                 | 3        | (0 0 15) |
| 5      | 48.755    | 1.82              | 1.866    | 0.471         | 30                 | 6        | (2 0 5)  |
| 6      | 56.093    | 1.609             | 1.638    | 0.453         | 20                 | 3        | (0 2 10) |

The calculated Average values are given as below

A. For Hexagonal lattice

$$a_H = 4.54 \text{ \AA}$$

$$c = 11.86 \text{ \AA}$$

B. Rhombohedral lattice

$$a_R = 4.74 \text{ \AA}$$

$$\alpha = 57.18^\circ$$

The above values were founded to be in good agreement with the corresponding standard values<sup>26</sup>.

The lattice parameters for the rhombohedral lattice of bismuth telluride were also calculated by a procedure similar to the one adopted for bismuth.

The calculated average values are given as below

A. For Hexagonal lattice

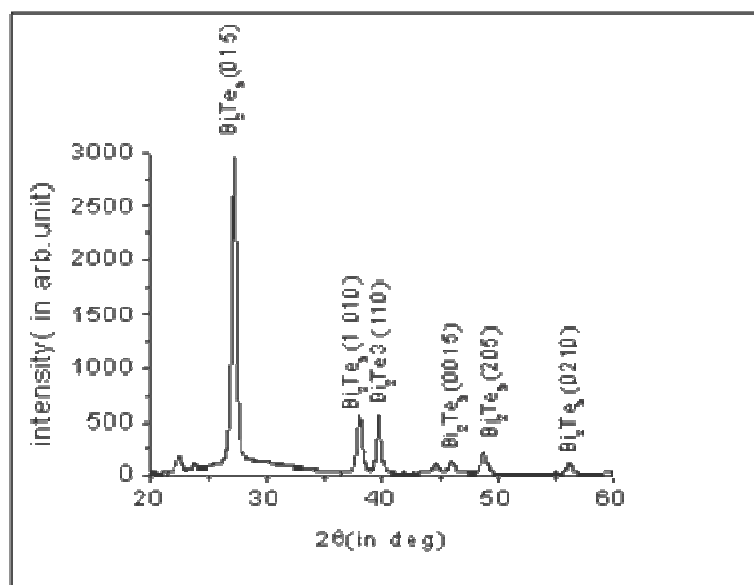
$$a_H = 4.54 \text{ \AA}$$

$$c = 29.71 \text{ \AA}$$

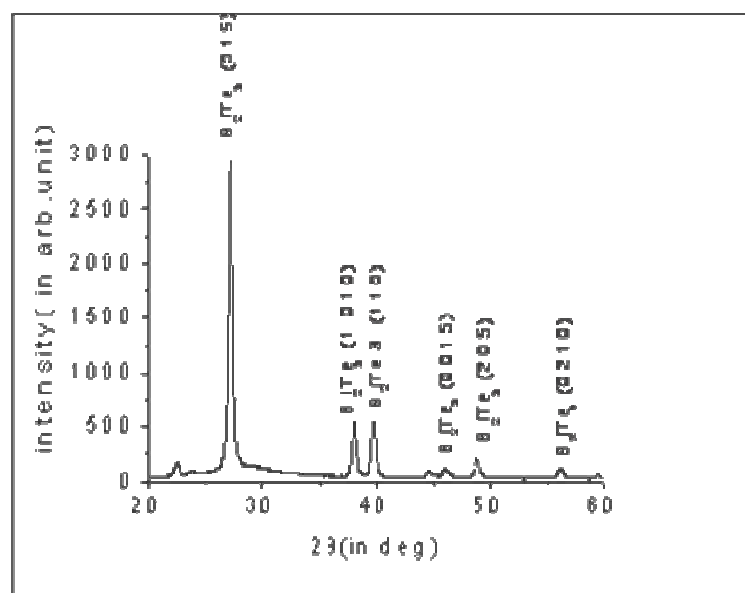
B. Rhombohedral lattice

$$a_R = 10.24 \text{ \AA}$$

$$\alpha = 25.60^\circ$$



**Fig-7. Typical GAXRD data recorded for  $\text{Bi}_2\text{Te}_3$  film Electrodeposited**



**Fig- 8. Typical GAXRD data recorded for  $\text{Bi}_2\text{Te}_3$  film electrodeposited at - 0.95 V.**

**Table 3.**  
The observed values of  $2\theta$ ,  $d$ , FWHM and peak intensities along with the standard values for films of Bi<sub>2</sub>Te<sub>3</sub> electrodeposited at -0.95V.

| S. no. | $2\theta$ (Degree) | d-value  |          | FWHM (Degree) | Intensity |          | (hkl)    |
|--------|--------------------|----------|----------|---------------|-----------|----------|----------|
|        |                    | Standard | Observed |               | Standard  | Observed |          |
| 1.     | 22.386             | 3.76     | 3.83     | 0.4400        | 5         | 5        | (101)    |
| 2.     | 27.126             | 3.23     | 3.28     | 0.4360        | 100       | 100      | (0 1 5)  |
| 3.     | 37.936             | 2.36     | 2.37     | 0.4190        | 70        | 27       | (1 0 10) |
| 4.     | 39.605             | 2.21     | 2.27     | 0.3973        | 50        | 31       | (1 1 0)  |
| 5.     | 44.648             | 1.99     | 2.02     | 0.5507        | 30        | 18       | (0 0 15) |
| 7.     | 48.700             | 1.82     | 1.86     | 0.4469        | 30        | 11       | (2 0 5)  |
| 8.     | 56.00              | 1.67     | 1.64     | 0.3600        | 5         | 8        | (1 0 16) |

The lattice parameters for the rhombohedral lattice of bismuth telluride were also calculated by a procedure similar to the one adopted for bismuth.

The calculated average values are given as below

A. For Hexagonal lattice

$$a_H = 4.54 \text{ \AA}$$

$$c = 29.83 \text{ \AA}$$

B. Rhombohedral lattice

$$a_R = 10.28 \text{ \AA}$$

$$\alpha = 25.53^\circ$$

From the above studies it can be concluded that non-aqueous ethylene glycol based bath can be successfully used for electrodeposition of bismuth, tellurium as well as their compound bismuth telluride. The cyclic voltametry studies performed in the baths containing bismuth & tellurium ions separately as well as together, have been used to identify the potential where codeposition of both the species may occur. This potential has been identified as between -0.9 to -0.95 V. The electrodeposited Bi, Te as well as Bi<sub>2</sub>Te<sub>3</sub> films have been shown to be single phase & polycrystalline in nature. The Bi<sub>2</sub>Te<sub>3</sub> films have also been shown to

possess a rhombohedral (hexagonal) structure with strong (015) orientation.

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